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(21) International Application Number: PCT/US00/08951 (22) International Filing Date: 5 April 2000 (05.04.00) (30) Priority Data: 09/287,432 7 April 1999 (07.04.99) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: MORI, Hiroshi; 1-1-11-301, Izumigaoka, Ut-sunomiya-shi, Tochigi 321-0952 (JP). KASSAL, Robert, James; 609 Westmond Drive, Wilmington, DE 19808 (US). SHINOHARA, Kenichi; 2-32-5, Toyosatodai, Ut-sunomiya-shi, Tochigi 302-0003 (JP). (74) Agent: JOUNG, J., Kenneth; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYACETAL RESINS WITH REDUCED FORMALDEHYDE ODOR (57) Abstract Incorporation of an odor-reducing additive selected from the group consisting of: (i) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of P _{kb} in the range of 2 - 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and mixtures thereof, into a polyacetal resin to reduce its formaldehyde odor. A combination of the odor-reducing additive with a weak acidic imino was found to have a synergistic effect in further reducing the formaldehyde odor.		

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POLYACETAL RESINS WITH REDUCED
FORMALDEHYDE ODOR

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a novel polyacetal resin composition, and articles molded therefrom, which has excellent heat stability, air oven aging and moldability as well as a considerably reduced formaldehyde odor for packaged resins and molded parts.

Background

10 Polyacetal resins, which are prepared by polymerizing a starting material mainly comprising formaldehyde monomer or trioxane, a trimer of formaldehyde, exhibit excellent mechanical and physical properties, such as tensile strength, stiffness, as well as fatigue resistance, sliding resistance, chemical resistance, and the like. The resins are used extensively in various applications as an engineering
15 plastic material due to their excellent physical properties (such as mechanical and electrical properties) and chemical properties. However, the resins at times may evolve traces of formaldehyde from which they were made, even at room temperature. Similarly, molded articles made from polyacetal resins may also evolve traces of formaldehyde, which may make molded parts to be less desirable
20 in some circumstances.

US Patent No. 5,866,671 discloses polyacetal compositions containing acidic hydantoin and imidazole derivatives with reduced odor levels.

There is still a demand for means to reduce the formaldehyde odor in polyacetal resins as well as that which may arise in articles molded from
25 polyacetal resins.

SUMMARY OF THE INVENTION

The present inventors have surprisingly found a novel composition comprising:

- a) a polyacetal resin; and
- 30 b) a sufficient amount of at least an odor-reducing additive to reduce the formaldehyde concentration of the resin to less than 50%. The odor-reducing additive is selected from the group consisting of: (i) a low molecular weight primary or secondary amino compound of low volatility, containing at least one

amino group and two or more carbon atoms and having a weak basicity of P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and mixtures thereof.

The invention also relates to a novel composition comprising: a) a polyacetal resin; a sufficient amount of at least b) an odor-reducing additive selected from the group consisting of: (i.) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid; and c) a weak acidic organic cyclic compound having an active imino, to provide a synergistic effect in reducing the formaldehyde odor of at least in half.

DETAILED DESCRIPTION OF THE INVENTION

Polyacetal Resins

The polyacetal base resin that may be used in the compositions of the present invention is a high-molecular weight polymer comprised of repeating oxymethylene units ($-CH_2O-$) which may be selected from among polyoxymethylene homopolymers, copolymers (including block copolymers) and terpolymers comprising oxymethylene units and a minor amount of other constituent units.

The polyacetals used in the compositions of the present invention may, moreover, be linear, branched or crosslinked, with terminal groups thereof being either not protected or being protected. The polyacetal resin will generally have a number average molecular weight in the range of 5,000 to 100,000, preferably 10,000 to 70,000. The molecular weight can conveniently be measured by gel permeation chromatography in m-cresol at 160° C. using a Du Pont PSM bimodal column kit with nominal pore size of 60 and 1000 Angstrom.

The polyacetal used in the present invention can be either a homopolymer, a copolymer or a mixture thereof. The preferred homopolymer is generally prepared by the polymerization of anhydrous formaldehyde or a cyclic trimer thereof, i.e., trioxane. Generally, the homopolymer is stabilized against thermal decomposition by end-capping with a suitable moiety having greater stability as compared to the oxymethylene units. The preferred copolymer on the other hand is

a high-molecular weight polymer comprising between about 85 to 99.9% of repeating oxymethylene units randomly interspersed with higher oxyalkylene units (e.g., having two or more adjacent carbon atoms).

Copolymers can contain one or more comonomers, such as those generally used in preparing polyacetal compositions. Comonomers more commonly used include alkylene oxides of 2-12 carbon atoms and their cyclic addition products with formaldehyde. The quantity of comonomer will not be more than 20 weight percent, preferably not more than 15 weight percent, and most preferably about 2 weight percent. The most preferred comonomer is ethylene oxide. Generally polyacetal homopolymer is preferred over copolymer because of its greater stiffness. Preferred polyacetal homopolymers include those whose terminal hydroxyl groups have been end-capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively.

Additives

The odor-reducing additives of the present invention include: i) a water-soluble, low molecular weight primary or secondary amino compound, containing at least one amino group and two or more carbon atoms and having a weak basicity of P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and mixtures thereof.

With respect to the water-soluble, low molecular weight primary or secondary amino compounds containing at least one amino group and two or more carbon atoms, no particular limitation is imposed on the number of amino group(s). The amino compounds can be an aliphatic, alicyclic, aromatic or heterocyclic group having two or more carbon atoms. The amino compounds may contain one or more groups other than amino group(s), for example, hydroxyl, ester, ether, carboxyl, carbonyl, amido, imido, sulfonic, carboxamido, imino and/or unsaturated groups.

The water-soluble, low molecular weight primary or secondary amino compounds are characterized by being weak bases, i.e., having have a basicity p_{kb} 's ranging from about 2 to 8, preferably being very weak bases, i.e., having have a basicity p_{kb} 's ranging from about 4 to 8.

The water-soluble, low molecular weight primary or secondary amino compounds are further characterized as having a low volatility, i.e., the boiling

point of the amino compounds should be as follows: $T_{bp} > T_m - 60^\circ\text{C}$, where T_{bp} is the boiling point of the amino compounds and T_m is the melting point of the polyacetal base resin.

Specific examples of such water-soluble, low molecular weight primary or secondary amino compounds include, but are not limited to, e.g.,
5 monoethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane, alkyl aminobenzoates such as ethyl p-aminobenzoate, methyl anthranilate and butyl m-aminobenzoate, 2-amino-2-ethyl-propanediol and 2-amino-2-methyl-propanol.

Tris(hydroxymethyl)aminomethane, ethyl p-aminobenzoate, 2-amino-2-ethyl-propanediol and 2-amino-2-methyl-propanol are preferred for use as water-soluble, low molecular weight primary or secondary amino compounds in
10 accordance with this invention. Tris(hydroxymethyl)aminomethane and ethyl p-aminobenzoate are most preferred.

The amount of the odor-reducing additives to be added to the compositions of the present invention should be in a sufficient amount to reduce the formaldehyde
15 level of the resin or its molded parts in half. The amount of additives is about 0.01 - 10 in parts by weight, preferably 0.02 - 5 by weight, and most preferably 0.05 - 2 parts by weight, per 100 parts by weight of the polyacetal resin.

Other Additives

20 The composition of the present invention can further contain, one or more ordinary additives including: lubricants; nucleating agents; mold release agents; antistatic agents; surfactants; organic polymeric materials; inorganic, organic, fibrous, granular or platy fillers, anti-oxidants, pigments, colorants, carbon black, reinforcing agents and fillers such as a glass fiber, etc., in such an amount as not to
25 negate the effects of this invention.

Representative lubricants that may be used include, but are not limited to, silicone types such as dimethylpolysiloxanes and their modifications; oleic acid amides; alkyl acid amides, e.g., stearic acid amide types; bis-fatty acid amid type lubricants such as bisamides; non-ionic surfactant type lubricants; hydrocarbon
30 type lubricants waxes, chlorohydrocarbons, fluorocarbons; fatty acid type lubricants including oxy-fatty acid; ester-type lubricants including lower alcohol esters of fatty acids; alcohol type lubricants including polyvalents, polyglycols, polyglycerols; and metal soaps such as lauric acid, stearic acid, etc., with metals.

Also, it is desirable to add antioxidant to prevent oxidative deterioration of the resin. Hindered phenol type antioxidants are preferred, and those antioxidants with melting point higher than 100°C, especially above 120°C, are most preferred.

5 It is also desirable to add heat stabilizers to the composition of this invention as formaldehyde scavengers such as: polyamide resins, amide compounds, urea derivatives and triazine derivatives.

Suitable polyamide resins include polyamide compounds, especially nylon terpolymers, hydroxy containing polymers, and nonmelting nitrogen or hydroxy
10 containing compounds, e.g., polyamide 6, polyamide 6/12 copolymer, polyamide 6/66/610 terpolymer, polyamide 6/66/612 terpolymer, ethylene-vinyl alcohol copolymer, acrylamide (co)polymer, acrylamide/N,N-methylenebis-acrylamide copolymer, stearic acid monoglyceride and poly beta alanine and the like.

Suitable amide compounds are stearic acid amide, oleic acid amide, erucic
15 acid amide, ethylenediamine-distearic acid amide, ethylenediamine-dibehenic acid amide, hexamethylenediamine-distearic acid amide, ethylenediamine-dioleic acid amide, ethylenediamine-dierucic acid amide, xylylenediamine-dierucic acid amide, di(xylylenediamine-stearic acid amide)sebacic acid and the like.

Suitable urea derivatives are N-phenylurea, N,N'-diphenylurea,
20 N-phenylthiourea, N,N'-diphenylthiourea and the like.

Suitable triazine derivatives are melamine, benzoguanamine, N-phenylmelamine, N,N'-diphenylmelamine, N-methylolmelamine, N,N'-trimethylolmelamine, 2,4-diamino-6-cyclohexyltriazine, and the like.

These heat stabilizer may be used individually or in combination. Of
25 these, nylon 66, poly-beta - alanine, ethylenediamine-distearic acid amide, ethylenediamine-dibehenic acid amide, ethylenediamine-dierucic acid amide, di(xylylenediamine-stearic acid amide)sebacic acid amide are preferred.

Preparation

The compositions of the present invention can be prepared by any means
30 of compounding. The additives can be added as dry powders, as concentrates ("master-batch"), as dispersions, or as solutions. One preferred method of incorporation involves adding the odor-reducing additives to polyacetal resin pellets to coat the pellets, and thereby mixing the mixtures in an extruder or

injection molder. In addition, the odor-reducing additives may be compounded into the polyacetal resin at the same time that other additives, such as thermal stabilizers, antioxidants, fillers, etc., are compounded therein. The additives may be added in the form of particle or in the molten state.

5 Molded parts of these polyacetal resin compositions may be formed by any molding process conventional in the plastics-forming art, including compression molding, vacuum forming, injection molding, extrusion molding, blow molding, rotary molding, melt spinning, and heat molding. Injection molding is especially preferred. During injection molding of the claimed compositions, mold deposits
10 attached to the mold were evaluated visually and were hardly observed or not found at all.

Examples

In the Examples and Comparative Examples, the characteristics of the acetal resin compositions and moldings were determined as follows:

15 Thermal Stability Test. Two grams of resin pellets were melted for 30 minutes at 250°C in a nitrogen atmosphere. The formaldehyde gas generated by the decomposition of the resin was introduced into a 4% aqueous sodium bisulfite solution, followed by titration with a 0.1 N hydrochloric acid (HCl). The amount of formaldehyde gas generated (TEF) is expressed by the following formula:

20 Amount of formaldehyde formed (%) = $30.03 \text{ NV/S} \times 100$

wherein V was the amount of HCl, in ml, required for titrating after 30 minutes, N was the normality, in ml, of HCl, S was the amount of sample, in grams, and 30.03 was the molecular weight of formaldehyde.

Odor Test 1 – Pellets: 100 g of resin pellets were sealed in a 300 ml
25 polyethylene containers and kept at various temperatures: room temperature, 50°C and 80°C. At the start of the test, then after 1 and 2 hours respectively, 10 ml of gas was removed from the containers using a syringe and formaldehyde concentration was measured using a gas-phase measuring device made by Lion Company called Formaldemeter Mark II.

30 Odor Test 2 – Pellets: Resin pellets were stored at room temperature in sealed 50-lb. bags made out of polyethylene. Gas samples were tested by removing 1cc. gas from the sealed bags and formaldehyde concentration was measured using the gas-phase measuring device Formaldemeter Mark II.

Odor Test 3 – Molded Tensile-bar tests: 1/16" Tensile-bars were molded from a control composition as well as the claimed compositions. The tensile bars were stored at room temperature in sealed 1 gallon polyethylene containers. Gas samples were tested by removing 1cc. gas from the sealed containers and
5 formaldehyde levels were measured using a Formaldemeter Mark II.

Odor Test 4 – Molded part test: molded parts were molded from the claimed compositions, kept in sealed 300 ml polyethylene containers at various temperatures: 50°C and 80°C. Gas samples were tested by removing 1cc. gas from the sealed containers and formaldehyde levels were measured using a
10 Formaldemeter Mark II by the Lion Company.

Components: The polyacetal resins used in the Examples below were:

1. Polyacetal A available from E. I. du Pont de Nemours and Company of Wilmington, Delaware, USA ("DuPont"), having a number average molecular weight of about 37,000;
- 15 2. Polyacetal B available from DuPont, having a number average molecular weight of about 30,000;
3. Polyacetal C also available from DuPont, having a number average molecular weight of about 77,000; and
4. Polyacetal D, available from Polyplastics, Japan, under the tradename
20 Duracon® M25.

The additives used in the Examples are as listed in the tables below. In the Examples, THAM is tris(hydroxymethyl)aminomethane, EPA is ethyl p-aminobenzoate, AEPD is 2-amino-2-ethyl-propanediol and AMP is 2-amino-2-methyl-propanol.

25 Preparations: The polyacetal resin was mixed with the additives in an extruder and the resultant resin was pelletized, and in some instances, formed into molded parts. The samples were evaluated by the Thermal Heat Stability test and the various Odor Tests. Comparative Examples were those obtained by processing similar polyacetal without any odor-reducing additives at all.

30 The results of evaluation are listed in the tables below, demonstrating that the examples using the additives of the present invention were able to suppress the formaldehyde odors in resin without severely adversely affecting the melt stability of the resins.

In the first set of experiments, polyacetal B was used and the formaldehyde levels were measured using the Thermal Stability test as well as the Odor Test 1 (pellets in 300 ml PE bottle):

Table 1

Example	Wt. % additive	Additive	TEF	ppm CHCHO ppm initial	ppm CHCHO 50°C /1hr	ppm CHCHO 80°C /1hr
Com 1-1	-	None	0.15	19.5	84	> 85
1-2	0.05	EPA	0.13	6.8	30.9	75.4
1-3	0.2	EPA	0.12	0.5	3.3	13.8
1-4	0.5	EPA	0.13	0.3	1.3	7.3
1-5	0.2	THAM	0.23	0.5	1.6	3.0

In the next set of experiments, polyacetal A was used and the formaldehyde levels were measured using the Thermal Stability test as well as the Odor Test 2 (50 lb. PE sealed bags).

Table 2

Example	Wt. % additive	Additives	TEF	Ppm CHCHO 19°C /3 day	Ppm CHCHO 23°C /7 day	ppm CHCHO 24°C/23 day
Compare 2-1	0.0	None	0.47	34.4	56.0	44.8
2-2	0.2	THAM	0.83	0.3	0.4	0.4
2-3	0.2	Theophylline	2.59	2.9	0.7	1.5
2-4	0.2	Succinimide	1.12	0.9	1.1	1.2
2-5	0.2	Anthranilamide	1.33	0.3	0.3	0.5
2-6	0.2	Glycine anhydride	-	7.6	12.0	15.1
2-7	0.2	Anthranilic acid	2.37	0.3	1.2	2.0
2-8	0.2	4-amino benzoic acid	-	1.6	5	13.1
2-9	0.2	Uracil	0.92	1.7	3.2	6.1
2-10	0.2	Barbituric acid	-	0.3	0.5	0.5

In the third set of experiments, polyacetals C and D were used and the formaldehyde levels were measured via Odor Tests 1 (pellets in 300 ml PE bottle):

Table 3

Example	Polyacetal Resin	Wt. % Additive	Additive	ppm CH2O 23C/ 1hr	ppm CH2O 50C/ 1hr	ppm CH2O 80C/ 1hr
Com 3-1	C	-	None	12.7	70.8	> 86
3-2	C	0.05	THAM	0.4	1.7	1.0
3-3	C	0.05	AMP	1.2	12.2	63.8
3-4	C	0.05	AEPD	0.4	2.0	2.8
3-5	D	0.05	THAM	0.1	1.9	2.0

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In table 4, polyacetal A was used and the formaldehyde levels were measured via Odor Tests 2 (50 lb. sealed bags) and 3 (tensile-bar samples). In some of the examples, an acidic organic cyclic compound having an active imino such as 5,5-dimethylhydantoin (DMH) was added to the additive of the present invention.

The combination of the odor-reducing additives of the invention with the weak acidic imino was found to have a synergistic effect in reducing formaldehyde odor:

Table 4

Example	Wt. % additive	Additive	TEF	ppm CH ₂ O 3 days	ppm CH ₂ O 7 days	ppm CH ₂ O 21 days	ppm CH ₂ O T-Bars 1 day
Corn 4-1	-	None	0.69	34.4	95.6	80	383.2
4-2	0.05	DMH	0.63	5.1	5.3	3.8	147
4-3	0.1	DMH	0.56	5.2	3.3	3	25.6
4-4	0.2	DMH	0.64	2.6	1.8	1.8	16
4-5	0.2	THAM	-	-	0.4	0.4	16
4-6	0.1	50% THAM/ 50% DMH	0.85	0.3	0.3	0.4	12.6
4-7	0.2	50% THAM/ 50% DMH	0.73	0.3	0.3	0.3	7.1

In another set of examples, polyacetal B was used and the formaldehyde levels were measured using Odor Test 1 (pellets in PE bottles):

Table 5

Example	Wt. % additive	Additive	ppm CH ₂ O 23C/ 1hr	ppm CH ₂ O 50C/1hr	ppm CH ₂ O 80C/ 1hr
Compare 5-1	-	None	19.5	84	> 85
5-2	0.05	ethyl p-aminobenzoate	6.8	30.9	75.4
5-3	0.2	ethyl p-aminobenzoate	0.5	3.3	13.8
5-4	0.5	ethyl p-aminobenzoate	0.3	1.3	7.3
5-5	0.2	DMH	0.8	3.9	16.6
5-6	0.2	THAM	0.5	1.6	3.0
5-7	0.1	THAM	0.5	1.4	3.3
5-8	0.1	50% THAM/50% DMH	0.5	4.7	11.7

The examples were repeated with 30 g of molding parts from polyacetal B, and the formaldehyde levels were measured using Odor Test 4 (molded parts in 300 ml PE bottle), confirming the synergistic effect of a combination of the odor-reducing additives of the invention with a weak acidic organic cyclic compound having an active imino such as 5,5-dimethylhydantoin (DMH):

Table 6

Example	Wt. % additive	Additive	Ppm CH ₂ O 50 C 1hr	ppm CH ₂ O 80 C 1 hr
Compare 6-1	-	None	53.8	> 85
6-2	0.05	Ethyl p-aminobenzoate	58.7	> 85
6-3	0.2	Ethyl p-aminobenzoate	45.2	60.9
6-4	0.5	Ethyl p-aminobenzoate	35.7	32.4
6-5	0.2	DMH	30.6	42.9
6-6	0.2	THAM	67.1	> 85
6-7	0.1	THAM	83	> 85
6-8	0.1	50% THAM/ 50% 5.5-DMH	10.4	38.1

As is apparent from the foregoing description, the materials prepared and
5 procedures followed relate only to specific embodiments of the broad invention.
While forms of the invention have been illustrated and described, modifications
can be made without departing from the spirit and scope of the invention.
Accordingly, it is not intended that the invention be limited thereby.

CLAIMS

What is claimed is:

1. A polyacetal resin composition comprising:
 - a) a polyacetal resin; and
 - 5 b) a sufficient amount of at least one odor-reducing additive selected from the group consisting of: (i) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and
- 10 mixtures thereof;
wherein said composition being characterized by having a formaldehyde concentration at room temperature of less than about 50% of the formaldehyde concentration of similar polyacetal compositions free of said odor-reducing additive or mixtures thereof.
- 15 2. The composition of Claim 1, wherein the water-soluble, low molecular weight primary or secondary amino compound containing at least one amino group and two or more carbon atoms has a weak basicity of P_{kb} in the range of about 4 – 8.
- 20 3. The composition of Claim 1 wherein the polyacetal resin is an acetal homopolymer.
4. The composition of Claim 1 wherein the polyacetal resin is an acetal copolymer.
- 25 5. The composition of Claim 1 wherein the water-soluble, low molecular weight amino compound is selected from the group consisting of 2-amino-2-ethyl-propanediol, 2-amino-2-methyl-propanol, tris(hydroxymethyl)aminomethane, ethyl p-aminobenzoate, and mixtures thereof.

6. The composition of Claim 5 wherein the water-soluble, low molecular weight amino compound is selected from the group consisting of:

tris(hydroxymethyl)aminomethane, ethyl p-aminobenzoate, and mixtures thereof.

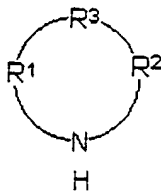
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7. The composition of Claim 5 wherein the odor-reducing additive is present in an amount of about 0.01 -10 in parts by weight.

8. The composition of Claim 1, wherein the water-soluble, low molecular weight amino compound has a boiling point of: $T_{bp} > T_m - 60^\circ\text{C}$, where T_{bp} is the boiling point of the amino compound and T_m is the melting point of the polyacetal base resin.

10

9. The composition of Claim 1, further comprising an organic cyclic compound having an active imino group according to the formula:



15

wherein R^1 , R^2 , and R^3 represent divalent organic radicals, and

wherein said organic cyclic compound having an active imino group is present in an amount sufficient for said composition to have a formaldehyde concentration at room temperature of about less than 50% of the formaldehyde concentration of similar polyacetal compositions free of said odor-reducing additive and said organic cyclic compound having an active imino group.

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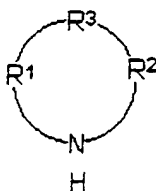
10. The composition of Claim 1, further containing at least one other customary additive selected from the group consisting of stabilizers, impact modifiers,

reinforcing agents, anti-statics, antioxidants, plasticizers, lubricants, fillers, and colorants.

11. A shaped article produced from the composition of Claim 1.
12. A method for reducing formaldehyde concentration from a molded part comprising a polyacetal resin composition, said method comprising blending a polyacetal resin with a sufficient amount of at least one odor-reducing additive selected from the group consisting of: (i) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and mixtures thereof, forming a blend with a formaldehyde having a reduced formaldehyde concentration of about less than 50% of the formaldehyde concentration of similar polyacetal compositions free of said odor-reducing additive.
13. The method for reducing formaldehyde concentration of claim 12, wherein the a water-soluble, low molecular weight primary or secondary amino compound containing at least one amino group and two or more carbon atoms has a weak basicity of P_{kb} in the range of about 4 – 8.
14. The method for reducing formaldehyde concentration of claim 12, further comprising shaping said blend into a molded part by injection molding, blow molding, extrusion or coextrusion molding, compression molding, rotary molding, melt spinning, heat molding, or vacuum forming.
15. The method for reducing formaldehyde concentration of claim 12, wherein the water-soluble, low molecular weight amino compound is selected from the group

consisting of: 2-amino-2-ethyl-propanediol, 2-amino-2-methyl-propanol, tris(hydroxymethyl)aminomethane, ethyl p-aminobenzoate, and mixtures thereof.

16. The method for reducing formaldehyde concentration of claim 12, wherein the water-soluble, low molecular weight amino compound has a boiling point of: $T_{bp} > T_m - 60^\circ\text{C}$, where T_{bp} is the boiling point of the amino compound and T_m is the melting point of the polyacetal base resin.
17. The method for reducing formaldehyde concentration of claim 12, wherein the odor-reducing additive is present in an amount of about 0.01 – 10 in parts by weight.
18. The method for reducing formaldehyde concentration of claim 12, further comprising the step of blending said polyacetal resin with a sufficient amount of at least one organic cyclic compound having an active imino group according to the formula:



- wherein R^1 , R^2 , and R^3 represent divalent organic radicals, and wherein said organic cyclic compound having an active imino group is present in an amount sufficient for said composition to have a formaldehyde concentration at room temperature of about less than 50% of the formaldehyde concentration of similar polyacetal compositions free of said odor-reducing additive and said organic cyclic compound having an active imino group.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/08951

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/00 C08L59/00 //(C08K5/00,5:17,5:3445)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 15 69 286 A (DU PONT DE NEMOURS) 3 July 1969 (1969-07-03) example 1; table 1	1-8, 10, 12-17
A	GB 996 252 A (ASAHI KASEI KOGYO KABUSHIKI KISHA) 23 June 1965 (1965-06-23) claims; examples	9, 18
A	DATABASE WPI Section Ch, Week 199642 Derwent Publications Ltd., London, GB; Class A25, AN 1996-422125 XP002142074 & JP 08 208946 A (DAINICHISEIKA COLOR & CHEM MFG), 13 August 1996 (1996-08-13) abstract	1-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

information on patent family members

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